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Preliminary communication

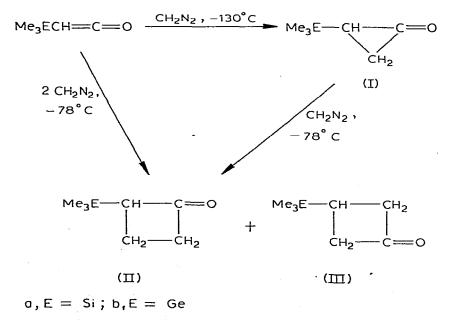
SILYLATED AND GERMYLATED CYCLOPROPANONES

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Summary

The synthesis of trimethylsilyl- and germyl-cyclopropanones, by treating diazomethane with the corresponding trimethyl ketene, and their ring expansion to cyclobutanones are described.

Earlier we reported [1] the synthesis, relative stability, and isomeric and tautomeric transformations of O- and C-silylated or -germylated monocarbonyl compounds. We are now studying the relative stability of the isomers as a function of, in particular, ring size of the element-substituted ring ketones.

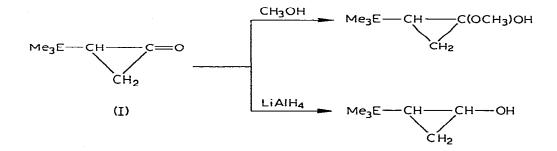


SCHEME 1

Accordingly, we have synthesized some of these compounds by a reaction of silyl- or germylketenes with diazomethanes. The reaction is carried out with a solution of diazomethane in ether or methylene chloride at -130° C. Slow addition of diazomethane to an equimolar amount of trimethylsilylketene leads to trimethylsilylcyclopropanone (Ia, yield 50%, b.p. $34-35^{\circ}$ C/6 mmHg, n_D^{20} 1.4428, ν (C=O) 1815 cm⁻¹). Trimethylgermylcyclopropanone (Ib, yield 50%, b.p. $45-47^{\circ}$ C/5 mmHg, n_D^{20} 1.4632, ν (C=O) 1810 cm⁻¹) has been obtained in a similar way. PMR spectra of the compounds (Ia, Ib) contain an ABC system of cyclopropane ring protons at δ 0.8–1.8 ppm.

The products obtained react with diazomethane to result in ring expansion leading to the formation of a mixture of the isomeric element-substituted cyclobutanones II and III. These have also been synthesized by treating silyl and germyl ketenes with an excess of diazomethane at -78°C. Similar compounds were obtained previously [2] by treating excess diazomethane with triethylgermylketene at 0°C (scheme 1).

Addition of methanol to the carbonyl group cyclopropanones (I) readily results in almost quantitative yields of the products. The compounds I may be smoothly reduced to the respective element-substituted cyclopropanols by lithium aluminium hydride.



All elemental analyses are satisfactory. The structures have been verified by IR and PMR data.

References

1 Yu.I. Baukov and I.F. Lutsenko, Organometal. Chem. Rev. A, 6 (1970) 355.

2 A. Laporterie, Small Thesis, University of Toulouse, France, 1968.